(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 246 205 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
02.10.2002 Bulletin 2002/40

(51) Int Cl.[7]: **H01B 1/12**, H01B 1/20, H01B 1/24, H01B 1/22

(21) Application number: **01810304.4**

(22) Date of filing: **26.03.2001**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant: **ABB RESEARCH LTD.**
8050 Zürich (CH)

(72) Inventors:
- **Dirix, Yvo**
  8057 Zürich (CH)
- **Fuhrmann, Henning**
  8047 Zürich (CH)
- **Greuter, Felix**
  5406 Baden-Rüthihof (CH)
- **Paul, Willi**
  5430 Wettingen (CH)
- **Carlen, Martin**
  5443 Niederrohrdorf (CH)

(74) Representative: **ABB Patent Attorneys**
c/o ABB Schweiz AG
Brown Boveri Strasse 6
5400 Baden (CH)

(54) Electrically conducting nanocomposite material

(57) An electrically conducting nanocomposite material with a matrix comprising an intrinsically conducting polymer (ICP) and a plurality of conducting metaloxide (MO) nanotubes forming a threedimensional interconnected network embedded in the matrix is proposed. The nanotubes are furthermore coated with a metallic layer, and the interconnected network may be anisotropic via an at least partial alignment of the nanotubes.

EP 1 246 205 A1

Description

1. Field of the invention

[0001] The invention relates to composite materials that consist of metaloxide (MO) nanotubes or carbon nanotubes (CNT) with an intrinsically conducting polymer (ICP).

2. Description of the Prior Art

[0002] Since the discovery of CNTs in 1991, a lot of research has been devoted to the production and characterisation (purification) of these materials. Interesting physical and mechanical (stiffness/strength) properties have been reported for tubes, in particular very high electrical conductivities for individual nanotubes (10^3-10^4 S/cm). However, to benefit from these properties on a macroscopic scale, research has been focussed on incorporation of these carbon nanotubes in a polymeric matrix. For example electrically insulating matrix materials such as epoxies or polyvinylalcohol have been used. The electrical conductivity at room temperature remained however low ($< 10^{-4}$ S/cm at a filling grade of 0.1 vol. %), presumably due to the hindered charge transfer between individual nanotubes. The hindered charge transfer was reduced significantly by using intrinsically conducting (π-conjugated) polymers such as poly(p-phenylene vinylene) (PPV), resulting in an electrical conductivity at room temperature of 8.3 S/cm. However, the morphology of these materials is not homogeneous and consist of a bi-layer structure where the intrinsically conducting polymer is cast on top of a carbon nanotube layer which reduces the electrical conductivity of the composite.

3. Disadvantages of the prior art

[0003] First, the composites produced so far contained relatively expensive carbon nanotubes, this in contrast to metaloxide nanotubes, comprising for example vanadiumoxide, that are cheaper and available on a larger (Kgs) scale [WO9826871]. Secondly, the composites were fabricated from non-coated nanotubes whereas tubes coated with a metallic layer (silver, gold, nickel, copper) could further reduce the interface limitation hindering electrical charge transport between the tubes.

[0004] Additionally, the current carbon nanotube composites based on intrinsically conducting polymers consist of a bilayer structure whereas a co-continuous morphology would further improve the electrical conductivity of the material. Finally, the composites are isotropic, thereby not taking fully benefit from the highly anisotropic properties of the nanotubes.

4. Summary of the Invention

[0005] In the present invention , electrically conducting nanocomposites are proposed with an enhanced electrical performance which are based on nanotubes and intrinsically conducting polymers. These composites can be either isotropic or anisotropic. In the latter case the microscopic anisotropy (electrical/thermal/mechanical) of the tubes is transferred to a macroscopic scale. The composite structure is co-continuous and the nanofiller is either a carbon nanotube or a metaloxide nanotube such as vanadiumoxide, tinoxide, titaniumdioxide. Examples for the intrinsically conducting polymer are PPV, Polyaniline, polypyrolle, polythiophene or polyalkyl thiophenes, poly(p-phenylene ethynylene). Furthermore, the nanotubes can be used in its pure form or they can be coated either with an electrically conducting metallic layer or with a dopant layer. This layer can melt, diffuse or react during composite fabrication and thus form conducting or semi-conducting bridges between individual nanotubes in he composite material. This further reduces the electrical resistance at tube-tube contacts, in addition to the beneficial influence from the ICP matrix. The coating on the nanotubes can also be a (bifunctional) coupling agent which improves wetting and bonding of the nanotubes to the ICP matrix, thereby improving the processing, filling content, mechanical and electrical properties of the composite material. Both the the conducting ICP matrix and the coating are thought to serve as a bypass at local, low conductivity spots in the composite.

[0006] The ICP matrix comprises for instance a thermosetting polymer such as epoxy. The nanotubes are added in a sufficient amount to the thermosetting polymer and well distributed by appropriate means. After that, the thermosetting polymer is cured under heat and/or pressure, thereby forming a solid composit material comprising a threedimensional network of interconnected nanotubes embedded in the cured polymer matrix. Alternatively, the nanotubes can be distributed in the liquid or molten phase of a thermoplastic polymer prior to solidification. The nanotubes can be at least partially oriented in a preferential direction by applying suitable electromagnetic fields during the curing or solidification process or by solid state drawing of the solidified composite material, i.e. by mechanical deformation of the composite material at temperatures close to but below the melting temperature of its thermoplastic matrix. The resulting network of the interconnected nanotubes as well as the resulting composite show strong anisotropic properties.

Claims

1. Electrically conducting nanocomposite material with a matrix comprising an intrinsically conducting polymer and a plurality of conducting nanotubes

embedded in the matrix, **characterized in that** the nanotubes form a threedimensional interconnected network.

2. Nanocomposite material according to claim 1, **characterized in that** the nanotubes are at least partially coated with a metallic layer.

3. Nanocomposite material according to claim 1, **characterized in that** the network is anisotropic.

4. Process for producing an electrically conductive nanocomposite material with a matrix comprising an intrinsically conducting polymer and a plurality of conducting nanotubes embedded in the matrix, **characterized in that** the nanotubes are dispersed in a molten thermoplastic polymer or an uncured thermosetting polymer.

5. Process according to Claim 4, **characterized in that** the nanotubes are oriented by the application of external fields during curing or solidification of the matrix or by solid-state drawing.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 81 0304

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	K YOSHINO, H KAJII, H ARAKI, T SONODA, H TAKE, S LEE: "Electrical and Optical Properties of Conducting Polymer-Fullerene and conducting Polymer-Carbon Nanotube Composites" FULLERENE SCIENCE AND TECHNOLOGY, vol. 7, no. 4, 1999, pages 695-711, XP001025585 * page 695, paragraph 1 * * page 709, paragraph 3 * * page 707, paragraph 1 *	1	H01B1/12 H01B1/20 H01B1/24 H01B1/22
A	DATABASE WPI Section Ch, Week 198803 Derwent Publications Ltd., London, GB; Class A08, AN 1988-016671 XP002175949 & JP 62 277468 A (MITSUBISHI RAYON), 2 December 1987 (1987-12-02) * abstract *	1	
A	WO 99 05687 A (ZIPPERLING KESSLER) 4 February 1999 (1999-02-04) * claims 1-5 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7) H01B
A	EP 1 052 654 A (UNION CARBIDE) 15 November 2000 (2000-11-15) * page 4, line 46 - page 5, line 13; claims 9,10 *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	5 September 2001	Vanhecke, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 01 81 0304

This annex lists the patent family membersrelating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

05-09-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 62277468 A	02-12-1987	NONE	
WO 9905687 A	04-02-1999	EP 1002322 A	24-05-2000
EP 1052654 A	15-11-2000	JP 2000357419 A	26-12-2000

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82